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DESCRIPTION

~~EXTREMELY FINE SHAPE MEMORY ALLOY~~ WIRE, COMPOSITE ~~MATERIAL USING THE SAME~~, AND PROCESS FOR PRODUCING THE SAME

TECHNICAL FIELD

The present invention relates to an extremely fine shape memory alloy wire, a composite material using the same, and a process for producing the same.

BACKGROUND ART

It has been confirmed that products having a vibration-controlling function and exhibiting a retarded fatigue crack-developing rate can be obtained by embedding pre-strained shape memory alloy wires in a matrix of a carbon fiber reinforced plastic (CFRP), a glass fiber reinforced plastic (GFRP), aluminum (Al), or the like. These products utilize an effect that an elongation strain imparted to the wires beforehand in a low temperature martensitic phase state remains after only removal of the stress and that the wires are reverse-transformed into an austenitic phase by heating after molding so that the wires can restore the original shapes.

We have proposed a shape memory alloy wherein, by elevating the reverse transformation temperature of a TiNi wire having a diameter of 0.4 mm to the curing temperature (about 130°C) of a matrix material such as an epoxy resin by a cold drawing work, the TiNi wire can be easily embedded in a resin without causing any reverse transformation and any shrinkage of the TiNi wire during the curing even when the TiNi wire is not fixed at the both ends (WO 02/097149 A1).

However, this technique can be applied to only composite materials which cure at 130°C. Namely, the technique cannot be applied to heat-resistant CFRP and

GFRP to be molded at about 180°C, which are the most important in aviation and space industries.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a wire comprising a shape memory alloy in a martensitic phase which assumes an austenitic phase or a martensitic phase through phase transformation temperatures, which is capable of conjuncting with a resin at a high molding temperature of about 180°C, wherein the shape memory alloy comprises a TiNi alloy in an Ni content of 49 to 52% by atom, a composite material which comprises a resin comprising the wire, and a process for producing the same.

As a result of extensive studies for solving the above problems, the present inventors have found that an extremely fine wire having a diameter of 60 μm or less, which is formed by a cold drawing work of a wire of the above shape memory alloy, is capable of easily conjuncting with a resin even at a high molding temperature of 180°C or higher. Based on this finding, they have accomplished the present invention.

Namely, according to the present invention, the following shape memory alloy wires, composite materials, and processes for producing the composite materials are provided.

(1) A shape memory alloy wire subjected to a cold drawing work, which comprises a shape memory alloy in a martensitic phase which assumes an austenitic phase or a martensitic phase through phase transformation temperatures, has a diameter of 60 μm or less, has a reverse transformation starting temperature of 130°C or higher and a reverse transformation termination temperature of at least 250°C, and has a shrinking strain of 2% or more, wherein the shape memory alloy comprises a TiNi alloy in an Ni content of 49 to 52% by atom.

(2) The shape memory alloy wire according to the above (1), which has a cold drawing rate of at least 20%.

(3) A composite material which comprises a fibrous material and a resin, wherein the fibrous material comprises the shape memory alloy wire according to any one of the above (1) to (2).

(4) A composite material which comprises a fibrous material and a resin, wherein the fibrous material comprises the shape memory alloy wire according to any one of the above (1) to (2) and at least one fiber selected from a glass fiber and a carbon fiber.

(5) The composite material according to the above (3) or (4), wherein the resin comprises a thermosetting resin or a thermoplastic resin.

(6) The composite material according to the above (3) or (4), wherein the resin comprises a precured material of a thermosetting resin.

(7) The composite material according to the above (3) or (4), wherein the resin comprises a thermoset product of a thermosetting resin.

(8) The composite material according to any one of the above (3) to (7), wherein the thermosetting resin comprises an epoxy resin.

(9) A composite material which comprises a cured resin comprising the shape memory alloy wire according to any one of the above (1) to (2), wherein the shape memory alloy wire is heated to a temperature of a reverse transformation termination temperature thereof or higher to generate a contractive force.

(10) The composite material according to the above (9), which comprises at least one fiber selected from a glass fiber and a carbon fiber together with the shape memory alloy wire.

(11) The composite material according to (9) or (10), wherein said heating of the shape memory alloy wire is carried out by application of electric current to the wire.

(12) A process for producing a composite material, which comprises heat-curing a thermosetting resin or a precured material thereof comprising the shape memory alloy wire according to any one of the above (1) to (2) at a temperature which is a reverse transformation starting temperature of the shape memory alloy wire or higher and is lower than the reverse transformation termination temperature; and then heating at least a part of the shape memory alloy wire to a temperature of its reverse transformation final temperature or higher.

(13) The process according to the above (12), wherein the thermosetting resin or the precured material thereof comprises at least one fiber selected from a glass fiber and a carbon fiber.

(14) The process according to the above (12) or (13), wherein said heating of the shape memory alloy wire is carried out by application of electric current to the wire.

BEST MODE FOR CARRYING OUT THE INVENTION

The shape memory alloy (hereinafter also simply referred to as "alloy") for use in the present invention is an alloy in a martensitic phase which assume an austenitic phase or a martensitic phase through phase transformation temperatures. Such an alloy includes a TiNi alloy. In the TiNi alloy, the Ni content thereof is from 49 to 52% by atom (at%).

The shape memory alloy wire of the present invention is characterized in that the alloy wire is an extremely fine alloy wire having a diameter of 60 μm, which is formed by a cold drawing work of a wire of the above alloy, and the reverse transformation temperature thereof is at least 250°C.

In the extremely fine alloy wire, the diameter (thickness) is usually 60 μm or less, preferably 50 μm or less, and the lower limit is not particularly limited but is usually about 5 μm.

The reverse transformation starting temperature (As) of the alloy wire is usually 130°C or higher, preferably 132°C or higher, and the upper limit is usually about 140°C.

The reverse transformation termination temperature (Af) of the alloy wire is usually 250°C or higher, preferably 260°C or higher, and the upper limit is usually about 300°C.

The alloy wire of the present invention is one which has been subjected to a cold drawing work. In this case, the cold drawing work means that an alloy wire is drawn at a temperature of 0 to 30°C, preferably 0 to 20°C.

The cold drawing rate in the present specification means a cross-sectional area reduced rate of a drawn wire obtained by cold drawing of an alloy wire and is defined by the following equation:

$$R\ (\%) = (S^1 - S^2)/S^1 \times 100$$

R: cold drawing rate

S^1: cross-sectional area of alloy wire before the cold drawing work

S^2: cross-sectional area of alloy wire after the cold drawing work

In the alloy wire of the present invention, the cold drawing rate is at least 20%, preferably 30% or more, and more preferably 35% or more. The upper limit is usually about 50%. The As and Af of the alloy wire of the present invention can be controlled by the cold drawing rate, and the As and Af are also elevated according to increase of the cold drawing rate.

The alloy wire which has been subjected to a cold drawing work according to the present invention retains a substantial amount of shrinking strain (pre-strain). The shrinking strain is 2% or more, preferably 2.5% or more, and more preferably 3.5% or more, and the upper limit is usually about 4%. The shrinking strain can be controlled by the drawing rate at the cold drawing of the alloy wire.

Since the alloy wire of the present invention has been subjected to a cold drawing work, the yield stress thereof is very large. Therefore, it affords a resin/wire composite material having enhanced strength and rigidity at a low temperature.

The alloy wire in a martensitic phase of the present invention does not shrink substantially when heated at a temperature lower than the reverse transformation starting temperature (As) thereof but a phase change occurs when heated at a temperature of the reverse transformation termination temperature (Af) thereof or higher, so that the alloy wire is transformed to an alloy wire in an austenitic phase and shrinkage occurs. The alloy wire in an austenitic phase is again changed to a martensitic phase by cooling the wire to a low temperature. The As' and Af' in the alloy wire converted to the low-temperature martensitic phase is substantially the same as the As and Af in the alloy wire before the cold drawing work. Namely, in the alloy wire converted from the austenitic phase to the martensitic phase, the As' is about 20 to about 70°C and the Af' is about 30 to about 100°C. When the alloy wire in the low-temperature martensitic phase is heated at a temperature of the Af or higher, shrinkage occurs. The shrinkage in this case is nearly equal to that observed in a usual alloy wire in a martensitic phase.

In the alloy wire of the present invention, the temperature difference between the As and Af thereof is broad and the temperature difference is 130°C, preferably 150°C, and the upper limit is usually about 200°C. In the present invention, at the production of the composite material where the alloy wire of the present invention is arranged in a cured resin through conjunction of the alloy wire with a resin, a temperature between the As temperature and Af temperature of the alloy wire is adopted as a molding temperature (a temperature for conjunction). In the present invention, particularly, it is advantage to adopt a temperature which is 30 to 100°C, preferably 40 to 80°C, and more preferably 50 to 60°C, higher than the As temperature. Such a

molding temperature is a temperature lower than the Af temperature of the alloy wire and the alloy wire is in an intermediate state between a martensitic phase and an austenitic phase, and hence the shrinking rate thereof is low. Therefore, a deformation ratio of the composite obtained by conjunction of the alloy wire with a resin is very small and thus does not particularly hinder usefulness of the composite.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 and 2 are drawings showing measured results of a shrinking strain change involved in reverse transformation of a Ti-50 at% Ni wire with a cold drawing rate of 35%.

Fig. 1: wire having a diameter of 50 μm

Fig. 2: wire having a diameter of 40 μm

Fig. 3 is a drawing showing measured results of a shrinking strain change involved in reverse transformation of a Ti-50 at% Ni wire (diameter of 50 μm) which is subjected to thermal treatment at 130°C for 2 hours and has a cold drawing rate of 35%.

Fig. 4 is a drawing showing measured results of a shrinking strain change involved in reverse transformation of a Ti-50 at% Ni wire (diameter of 50 μm) which is subjected to thermal treatment at 180°C for 2 hours and has a cold drawing rate of 35%.

Figs. 5 and 6 are experimental results of a crack-suppressing effect detected when the alloy wire arranged in a composite material is heated by application of electric current.

Fig. 5 shows a shrinking strain change of the sample surface when an electric current is applied, and Fig. 6 shows a temperature change of the sample surface when an electric current is applied.

Specific meanings of the symbols in Figs. 1 to 4 are as follows:

As: a reverse transformation starting temperature from a martensitic phase to an austenitic phase formed when an alloy wire is heated in the direction of the arrow a.

Af: a reverse transformation termination temperature from a martensitic phase to an austenitic phase formed when an alloy wire is heated in the direction of the arrow a.

Ms: a reverse transformation starting temperature from an austenitic phase to a martensitic phase formed when an alloy wire is cooled in the direction of the arrow a.

Mf: a reverse transformation termination temperature from an austenitic phase to a martensitic phase formed when an alloy wire is cooled in the direction of the arrow a.

As': a reverse transformation starting temperature from a martensitic phase to an austenitic phase formed when an alloy wire is heated in the direction of the arrow b.

Af': a reverse transformation termination temperature from a martensitic phase to an austenitic phase formed when an alloy wire is heated in the direction of the arrow b.

With regard to the alloy wire having a diameter of 50 μm, in the case of the first heating-cooling cycle shown by the arrow a, the shrinking strain is 3.5%, As is 133°C, and Af is 267°C (Fig. 1).

On the other hand, with regard to the alloy wire having a diameter of 400 μm, in the case of the first heating-cooling cycle shown by the arrow a, the shrinking strain is 2.3%, As is 130°C, and Af is 210°C (Fig. 2).

From the above results, in the case of the extremely fine alloy wire (Fig. 1), at the same cold drawing rate of 35%, it is revealed that the shrinking strain increases to

3.5% and the reverse transformation temperature range becomes very broad and shifts to a high-temperature side.

On the other hand, in the second heating shown by the arrow b, in the case of the extremely fine alloy wire (Fig. 1), As' becomes 29°C, Af' becomes 67°C, and thus the reverse transformation temperature range returned to the same level as in the case of a usual thermally treated alloy wire.

Furthermore, a change of the shrinking strain involved in reverse transformation was investigated by measuring thermal expansion on the extremely fine alloy wires after thermal treatment at 130°C and 180°C each for 2 hours. The results are shown in Figs. 3 and 4, respectively. In the wire thermally treated at 130°C for 2 hours, it is revealed that the shrinking strain becomes about 3.0% and the reverse transformation temperature range becomes in the range of 160 to 264°C (Fig. 3).

On the other hand, in the wire thermally treated at 180°C for 2 hours, it is revealed that the shrinking strain becomes about 2.5% and the reverse transformation temperature range becomes in the range of 197 to 271°C (Fig. 4). From the results, in the alloy wire/resin composite material formed at 180°C, a shrinking strain of 2.5% still remains in the extremely fine wire. Thereby, it is considered that a restoring stress of 250 MPa or more is obtained.

Various alloy wire/resin composite materials can be obtained by the use of the alloy wire of the present invention.

The resin in this case includes a thermosetting resin and a thermoplastic resin. Examples of the thermosetting resin include an epoxy resin, a phenol resin, a polyimide resin, a vinyl ester resin, an unsaturated polyester resin, a polyurethane resin, a precured material of a thermosetting resin (thermosetting prepolymers), and the like. Examples of the thermoplastic resin include a polyolefin resin, a fluorine-containing

resin, a polyamide resin, a thermoplastic polyimide resin, a polyester resin, a polycarbonate resin, and the like.

The alloy wire for use in the composite material of the present invention can be used in combination with a conventionally known fibrous material, e.g., a glass fiber or a carbon fiber.

The composite material of the present invention can be a thermosetting material (pre-impregnation material) comprising the alloy wire and a thermosetting resin or a precured material thereof (prepolymer). The composite material can be any of various shapes such as sheet, thread, columnar, rope, and block shapes.

By heating the thermosetting composite material at a temperature lower than the Af of the alloy wire incorporated therein, usually a temperature of 185°C or lower to cure the resin, the material can be converted into a composite material comprising the alloy wire in the cured resin. In this case, the heating temperature is a temperature lower than the Af of the alloy wire, so that a large shrinkage of the alloy wire does not occur. Therefore, when the alloy wire of the present invention is used, it is actually not necessary to use both ends fixing apparatus which has been employed for retaining pre-strain of the wire in the cases of conventional alloy wires.

The composite material comprising the alloy wire of the present invention in the cured resin can express a shrinking force through phase change from a martensitic phase to an austenitic phase by heating at least a part of the alloy wire to a high temperature of the Af thereof or higher.

With regard to the product thus obtained, the alloy in an austenitic phase can be again converted into the alloy in a martensitic phase by further cooling the product to a low temperature. The product containing the alloy wire in a martensitic phase can be used in various applications utilizing characteristics of the alloy wire.

The composite material of the present invention can be a material formed by embedding the alloy wire in a thermosetting resin and heating it at a temperature lower than the Af to cure the resin. In this case, the resin can be a liquid one or a powdery one. Moreover, the resin can be one containing a fibrous material such as a glass fiber or a carbon fiber.

The composite material of the present invention can be a material formed by thermally melting a thermoplastic resin which melts at a temperature lower than the Af of the alloy wire and arranging the alloy wire therein, followed by cooling and solidification.

In the alloy wire in a martensitic phase which has undergone cold drawing and is incorporated in the composite material of the present invention, the As and Af thereof is not returned to normal ones unless the alloy is subjected to reverse transformation to an austenitic phase. Therefore, in the composite material, in order to obtain a shape-restoring power, it is necessary to heat the alloy wire in the composite material once to a temperature of the Af thereof or higher.

In the present invention, heating of the alloy wire incorporated in the above composite material can be advantageously carried out by passing an electric current through part or all of the alloy wire for a short period and then shutting down the application of electric current. In this case, the period of the application of electric current is from 1 to 60 seconds, preferably from 1 to about 20 seconds. Even when the alloy wire is heated to a temperature of the Af or higher by passing an electric current for such a short period, influence of the heat on the resin around the alloy wire is small. This is because the temperature of the alloy wire in the vicinity of the surface thereof is not immediately elevated since the reverse transformation is an endothermic reaction and the application of electric current is stopped while the surface temperature of the alloy wire is low.

By heating the alloy wire incorporated in the composite material to a temperature of the Af or higher and cooling it to a low temperature, the alloy wire is converted into a low temperature martensitic phase alloy wire, whose reverse transformation temperature returns to the normal one, and a shape-restoring power can be obtained by heating with a low current.

Example

The present invention is described below in detail based on Example.

Example 1

A Ti-50 at% Ni wire (diameter: 50 μm) having a cold drawing rate of 35% manufactured by a drawing work at a temperature of 15°C was kept at 180°C for 2 hours and embedded in a carbon fiber reinforced epoxy resin (CFRE) to prepare a composite material having damage-suppressing and vibration-controlling functions.

Since the molding conditions for CFRE in this case were at 180°C for 2 hours, the cold-drawn alloy wire was kept at 180°C for 2 hours and then, with regard to the resulting wire, the shrinking strain and change of the reverse transformation temperature were measured.

Fig. 4 shows the results. From Fig. 4, it was revealed that the cold-drawn wire retained a shrinking strain of 2.5% even when thermally treated at 180°C for 2 hours. According to this shrinking strain of 2.5%, a shape-restoring stress of 250 MPa or more can be obtained.

Figs. 5 and 6 shows experimental results on a crack-suppressing effect detected when the alloy wire in the composite material manufactured is heated by application of electric current. Fig. 5 shows a change of shrinking strain of the sample surface when an electric current is applied, and Fig. 6 shows a temperature change of the sample surface when an electric current is applied.

INDUSTRIAL APPLICABILITY

According to the present invention, there is provided a shape memory alloy wire advantageously applied to a resin having a high molding temperature of about 180°C, particularly a glass fiber reinforced resin and a carbon fiber reinforced resin. When the alloy wire is used, an alloy wire/resin composite material can be easily obtained without using a wire-both ends fixing apparatus for retaining pre-strain.

Since the alloy wire of the present invention has a diameter which is so extremely fine as 60 μm or less, it can be handled in a similar manner to conventional carbon fibers and glass fibers. Therefore, according to the present invention, a prepreg composite material wherein the alloy wire is incorporated in a thermosetting resin can be obtained.